

Is there still a Future for Hydrogenated Vegetable Oils?*

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catalysis · fatty acids · hydrogenation · nutrition · vegetable oil

1. Introduction

Catalytic hydrogenation of vegetable oils, viz. soybean oil, is an established technology in food industry.^[1] Its major concern is the hydrogenation of autoxidation-sensitive polyunsaturated fatty acid tails to stabilize the vegetable oil. Flash-hydrogenated oils find application in cold dressings and cooking oils. Somewhat deeper partial hydrogenation converts the vegetable oils into (semi-) solid fat products with different organoleptic and melting characteristics for use in various food applications, such as margarines and shortenings.

The catalytic hydrogenation of vegetable oils has a history of more than 100 years with fluctuating popularity, depending not only on economical factors but also on nutritional findings. For more than a decade, the use of industrially hydrogenated fats in food products was controversial because of the presence of *trans* fatty acid isomers. The presence of geometrical isomers is an inherent consequence of the Horiuti-Polanyi hydrogenation mechanism, which describes the stepwise and reversible addition of adsorbed hydrogen atoms to the adsorbed double bond on the catalyst surface.^[2] After reaction with one adsorbed hydrogen atom, a half-hydrogenated intermediate is formed, which is either reduced by the reaction with a second hydrogen atom, leading to the formation of a saturated bond, or it loses a hydrogen atom prior to desorption, potentially leading to the formation of geometric (*trans*) and positional isomers of the starting unsaturated fatty acid.

Although triglycerides that contain *trans* fatty acids have ideal melting characteristics, they are associated with a negative health impact,^[3] thus imposing the replacement of catalytic hydrogenation by other technologies, such as fractionation and catalytic interesterification, which yield “zero *trans*” fatty products.

The hydrogenation technology experiences industrial interest, because it allows the modification of fatty acid and

triglyceride compositions in a single step.^[4] As hydrogenation is a catalytic process, novel catalyst design is key to the production of (semi-solid) fats with acceptable organoleptic, melting, and nutritional properties, provided the “*trans* issue” can be circumvented. Other fat/oil applications, such as the production of essentially *trans*-free biolubricants and many renewable chemicals, could also benefit from new advances of catalytic vegetable oil hydrogenation.^[5]

The present essay reviews briefly the history of the catalytic hydrogenation of vegetable (edible) oils and illustrates how trends in food chemistry research converge with new nutritional insights. Certain novel promising catalytic developments, which were recently reported in this journal, are highlighted, such as the *trans*-free chemocatalytic hydrogenation, which shows unprecedented types of shape selectivity, and *trans*-selective enzymatic hydrolysis. This pioneering work uses new concepts, which could pave the way to alternatives to the nowadays prominently present palm-based shortenings. It illustrates that, 100 years after the first industrial production of hydrogenated fats for food products, selective hydrogenation of vegetable oils is still an exciting research domain of utmost importance for the food industry and beyond (Scheme 1).

2. Brief History

One of the first processes for liquid-phase hydrogenation of oleochemicals was introduced at the beginning of the twentieth century by Wilhelm Normann, a German chemist (1870–1939). Somewhat earlier, Paul Sabatier had demonstrated the hydrogenation in the vapor phase of unsaturated organic compounds with nickel metal. The hydrogenation of fatty oils was first patented by Normann in 1903.^[6] In 1906, the fat hydrogenation process was industrially implemented in England by Joseph Crossfield and Sons for the treatment of whale oil. Although initially aimed at the production of soaps, the hydrogenation technology was also used for manufacturing oil and fat products for food applications. By this technique, unstable fish and vegetable oils could be converted into stable and tasty margarines and shortenings.

The first all-vegetable hydrogenated fat, denoted as Crisco, was produced in 1911 by Procter & Gamble, who acquired the rights to the Normann patent in the US in 1909.^[7] Crisco, an acronym for crystallized cottonseed oil, shows

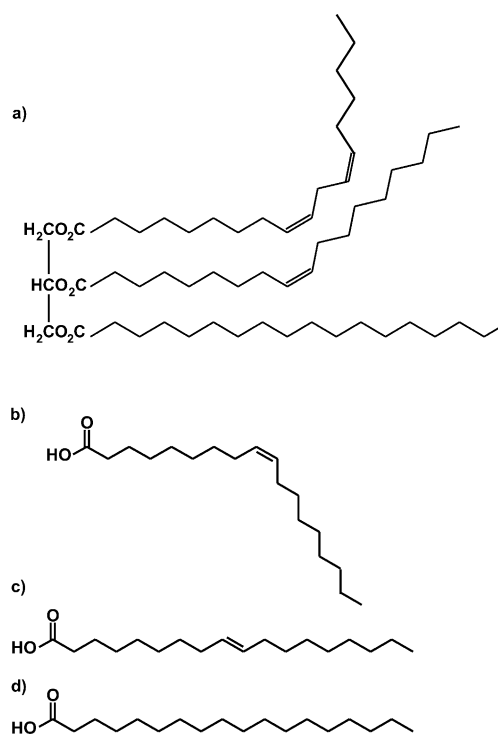
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physical properties similar to lard, which at that time was the preferred edible fat. This hydrogenated fat product, also known as “shortening”, was advanced as a “healthier” alternative to animal fats such as lard, resulting in a massive switch in consumption from animal fats into fatty products of vegetable origin. As the demand for these cheap animal fat substitutes continued to increase during the first decades of the twentieth century, the amount of industrially hydrogenated fats in foods increased rapidly. The popularity of hydrogenated fats for food applications caused even a patent conflict.^[8] In 1920, the US Supreme Court decided that claims 1 and 2 of the Burchenal patent were invalid, thus opening the way for other food processors to employ the hydrogenation process.^[9]

Already in 1922, Normann reported on the formation of various isomers of oleic acid during the hydrogenation of oils.^[10] Later, it was shown that these isomers are mainly positional C18:1 *trans* isomers of oleic acid, the most common ones being elaidic acid (C18:1 *trans*-9) and C18:1 *trans*-10.^[11]

From the early 1960s, research indicated a link between the intake of dietary saturated fatty acids and the occurrence of high levels of cholesterol in the blood, increasing the risk of cardiovascular diseases.^[12] As hydrogenated fats were a principal source of saturated fatty acids, the edible-oil industry



Scheme 1. Vegetable oils are a mixture of various triglyceride molecules (a), which contain three fatty acids, saturated and/or unsaturated, attached to a glycerol backbone. In nature, the double bonds in unsaturated fatty acids occur in *cis* configuration, as in oleic acid (C18:1 *cis*-9, b). During catalytic hydrogenation, geometrical *cis/trans* isomerization leads to the formation of *trans* fatty acids, such as elaidic acid (C18:1 *trans*-9, c), which has a linear structure similar to saturated fatty acids, such as stearic acid (C18:0, d).



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was forced to reformulate margarines and shortenings. To increase the ratio of polyunsaturated to saturated fatty acids, the oil industry switched from a single partially hydrogenated stock to a base stock system with formulated products by blending two or more stocks.^[13] This blending of a “soft” stock with a “harder” stock allows obtaining products with similar functionality as a single stock but with considerably higher levels of polyunsaturated fatty acids.^[1] Because of the “healthy” image of unsaturated fat products, more customers switched from the use of butter to margarine.

Since 1990, detrimental effects of *trans* fatty acids from industrially hydrogenated fats on blood lipids have been reported.^[3] Therefore governments have forced industry to reduce the amount of *trans* fats in food products. In 2003, Denmark was the first to implement legislation that limits the maximum level of *trans* isomers in edible fats to 2 wt %.^[14] In 2006, USA regulation introduced the labeling of the amounts of *trans* fatty acid in fats of food products, without imposing a complete ban. However, some US states endeavor essentially *trans*-free consumption goods.^[15] Very recently, the European Commission debated on the health issue of *trans* isomers and their presence in food.^[16] By December 2014, the commission committed to submit a report on the presence of *trans* fats in foods, accompanied with a legislative frame, if appropriate.

3. Rise of Tropical Oils

Because of the negative health effect of hydrogenated fats enriched in *trans* fatty acids and governmental pressures to reduce *trans* levels in food products, the food industry is gradually substituting modified tropical oils for hydrogenated fats. Tropical oils, such as palm and coconut oil, do not contain high levels of polyunsaturated fatty acids and hence do not require to be stabilized by the hydrogenation process. Moreover, *trans*-free fat products with desirable functionality can be obtained by tailoring the tropical oils with alternative processing technologies, such as fractionation and interesterification. Use of such techniques allows the tuning of the physical properties of naturally (oxidatively) stable oils for various applications by fractionating the oils based on their crystallization behavior and by randomizing the distribution of the fatty acids across the glycerol backbone. Currently these modified tropical oils, mainly palm oils, are common in shortenings (Table 1).

Although they are essentially *trans*-free, palm-based shortenings still contain high levels of saturated fatty acids (Table 1), mainly present as palmitic acid (C16:0). In bakery products, unhealthy *trans*-containing fats have been generally replaced by such highly saturated fats.^[18] As mentioned before, the presence of high levels of saturated fatty acids in the diet has been associated with the presence of high levels of cholesterol in the blood serum and consequently with an increased risk of cardiovascular health diseases (CHD).^[12] However, recent nutritional studies question this direct link between saturated fatty acids and an increased CHD risk.^[19] It is clear that the relationship of lipid intake to CHD risk is more complex than previously thought. Nevertheless, research in nutrition is continuously evolving and hence the knowledge on health influences of fats in diets will also undergo continuous changes.

4. Hydrogenated Fats with Low *trans* Levels

The availability of fats and oils is an important factor to determine their use in food industry, however, it can be difficult to predict, as it is not fully demand controlled. For example, soybeans are mainly planted for food purposes and some oil crops, such as sunflower and canola, are government controlled through subsidization. Geographically, palm oil almost exclusively comes from Southeast Asia, whereas soybean oil is mainly produced in the USA and South America. In Europe, the most important oil crops are sunflower and canola.^[20] It is obvious that all these variables affect availability, demand, and price.

Apart from tropical oils, most other important vegetable oils contain high levels of unsaturated fatty acids and therefore generally need to be stabilized against autoxidation. However, another elegant option is the use of trait-enhanced oils, such as sunflower oil with high levels of oleic acid.^[21] These variants contain much lower levels of linolenic and higher levels of oleic acid and hence possess a much higher oxidative stability, eliminating the need for further stabilization.

As most vegetable oils are liquid at room temperature, they need to be hardened to obtain fats with desired melting profiles for use in food products. It is therefore not unexpected to see a renewed interest by food producers in hydrogenated fat products and their production technology, provided very low levels of *trans* isomers, a good oxidation stability, and desired or tunable physical properties can be achieved.^[2b]

4.1. Hydrogenation that Produces Low *trans* Levels

Until today, significant efforts have been undertaken to reduce the formation of *trans* fatty acids during partial hydrogenation.^[22] One option is the hydrogenation under higher hydrogen pressure and at lower temperatures (Figure 1). Alternatively, a shift from traditional nickel catalysts to modified nickel^[22a] or even noble-metal catalysts is possible.^[22d,23]

Because of their reduced isomerization capability, catalysts based on noble metals lead to hydrogenated fats with a considerably reduced *trans*-isomer content compared with a nickel-based catalyst. However, these fats still contain substantial amounts of high-melting triglycerides (Figure 1) as a result of the low hydrogenation selectivity; the polyunsaturated fatty acids are not preferentially reduced to mono-unsaturated, but directly to saturated fatty acids. Especially the formation of high levels of fully saturated triglycerides (SSS) makes them unsuitable for most food applications because of undesired physical properties, for example, a sandy-mouth sensation. Figure 1 shows that it is not straightforward to design a hydrogenation process that combines low *cis/trans* isomerization with excellent (double bond) hydrogenation selectivities and therefore with low SSS selectivity. Moreover, properties such as catalyst porosity, dispersion of the hydrogenating metal on the catalyst support, and accessibility of the active metal centers for the bulky triglyceride molecules will determine hydrogenation activity and *cis/trans* isomerization selectivity. Therefore, the design of such a smart catalyst will not be an obvious thing to do.

Table 1: Content of *trans* and saturated fatty acids (SFA) of different commercial all-purpose shortenings.^[17]

Shortening ^[a]	<i>trans</i> [%]	SFA [%]	<i>trans</i> + SFA [%]
88 % H-SBO (IV 88) + 12 % 56-T Palm Oil	18.6	25.9	44.5
90 % H-CSO (IV 80) + 10 % 60-T CSO	9.5	34.4	43.9
35 % H-SBO (IV 96) + 55 % RB Palm Oil + 10 % 56-T Palm Oil	5.4	43.0	48.4
91 % RB Palm Oil + 9 % 56-T Palm Oil	0.0	54.5	54.5

[a] IV = iodine value; H = hydrogenated; SBO = soybean oil; CSO = cottonseed oil; RB = refined and bleached; T = titer.

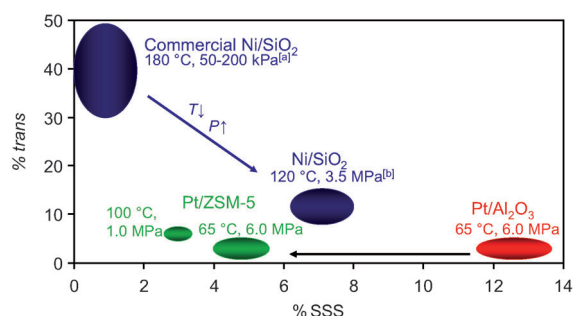


Figure 1. Selectivity of the formation of *trans* versus SSS (fully saturated triglycerides) of hydrogenated soybean oil with an iodine value (IV) of 65. The goal is to obtain hydrogenated fats that contain both low *trans* and low SSS levels, thus requiring a change of the nature of the catalyst and/or reaction conditions toward the origin of the graph. The commercial process (Ni/silica, 180 °C, 50–200 kPa) yields very low SSS levels, but very high *trans* levels. Lowering the temperature to 120 °C and increasing the pressure to 3.5 MPa results in lower *trans*, but higher SSS levels. Use of a Pt/Al₂O₃ catalyst yields very low *trans* and high SSS levels at low temperature (65 °C) and high hydrogen pressure (6.0 MPa). Using a Pt/ZSM-5 catalyst under the same conditions drastically lowers the SSS content without substantially increasing the *trans* content. Using Pt/ZSM-5 at 100 °C and 1.0 MPa yields a low *trans* and low SSS fat product. [a] After Ref. [23, 24]; [b] after Ref. [23]

Recent publications have demonstrated that *trans*-free hydrogenated products with excellent physical properties can be produced with a Pt/ZSM-5 catalyst, provided the Pt clusters are encapsulated in the pores of the ZSM-5 zeolite.^[25] The substitution of Ni with Pt in the catalyst formulation is important to substantially reduce geometrical isomerization, thus minimizing the formation of *trans* isomers, while for obvious geometric reasons the zeolite framework favors the selective hydrogenation of *trans* isomers over those with *cis* configuration.

Interestingly, the well-known low hydrogenation selectivity of Pt, reflected by the presence of high amounts of high-melting trisaturated triglycerides in the partially hydrogenated oil, is compensated by the preferred sorption on the surface of ZSM-5 of triglyceride molecules in tuning-fork configuration. This newly discovered type of shape selectivity involves a preference for hydrogenation of fatty acid chains located at the central (*sn*-2) position of the triacylglyceride. As a result of this type of pore mouth catalysis,^[25a] hydrogenated fats with a very low content of fully saturated triglycerides (SSS) are obtained (Figure 1). Although the importance of this unprecedented “positional selectivity” has been addressed before, it was considered negligible based on previously published articles.^[26] This positional selectivity has an important impact on the physical properties, such as the plasticity, of the hydrogenated fats.^[25b] Shape-selective hydrogenation of soybean oil samples thus delivers fat products with very low *trans* levels, but with desirable melting and crystallization properties.

The crucial role of the catalyst design in obtaining both excellent hydrogenation selectivity and low *trans* levels was also recently demonstrated by the use of a nanostructured catalyst with immobilized Pd.^[27] Vegetable oils were hydrogenated in THF/MeOH under a hydrogen atmosphere

(balloon) at room temperature with a high hydrogenation selectivity without *cis/trans* isomerization. Such a combination is uncommon for hydrogenations with Pd. The authors explained this remarkable result by a preferential entry of the hydrophobic tails of the triglyceride molecules into the Pd nanoclusters, when entrapped in organosilica sol-gel cages. Further research with nondiluted vegetable oils, combined with the (stereospecific) analysis of the triglycerides, could reveal the conceptual details even more firmly, in line with the Horiuti-Polanyi hydrogenation mechanism.

4.2. Selective Removal of *trans* Isomers

Another elegant novel strategy is the selective removal of *trans* isomers from partially hydrogenated fat by enzyme catalysis.^[28] In this work, a lipase with very high selectivity for the hydrolysis of linear (*trans* and saturated) fatty esters was prepared by protein engineering.

Some other earlier publications also dealt with this issue.^[29] For instance, a patent application that describes the selective removal of *trans* fatty acids from partially hydrogenated fat using a chemocatalytic approach was already issued in 1998.^[30] The ability of Pt-loaded zeolites to hydrogenate in a selective way *trans* fatty acid chains in triglyceride molecules was demonstrated. With such a Pt/zeolite catalyst, 15% of *trans* isomers of a diluted sample of partially hydrogenated rapeseed oil, which contains almost 50 wt % *trans* fatty acids, were saturated, hardly affecting (0.5 % conversion) the *cis* isomers present. This *trans*-selective hydrogenation was explained by the preferred adsorption into the micropores of the zeolite structure of the sterically less demanding linear chains of *trans* fatty acid over the bent chains of *cis* fatty acids. Actually, restricted adsorption in zeolites has been used for a long time in the petrochemistry for the production of *para*-xylene.^[31]

Such shape-selective sorption has been recently confirmed unambiguously for oleochemicals, such as methyl oleate (MO) and methyl elaidate (ME).^[29a] After a screening of different zeolite topologies and compositions, zeolite ZSM-5, which has pore sizes of about 0.55 nm and a Si/Al ratio of 140, appeared to be the sorbent of choice in the discrimination between MO and ME. The substantial difference in pore diffusivity between ME and MO was also exploited in the *trans*-selective hydrogenation of isomer mixtures of methyl esters, using a Pt-on-ZSM-5 catalyst. The concept of shape-selective hydrogenation is illustrated in Figure 2 for fatty acid methylesters (FAMES). Accordingly, *trans* FAMES were hydrogenated much faster than bent *cis* FAMES. Somewhat later, the same catalytic strategy was reported in this journal for the selective removal of *trans* fatty acids in model triglycerides.^[25a] Obviously, *trans*-selective hydrogenation will only be feasible if the Pt clusters are located in the zeolite pore structure. Consequently, the synthesis of the catalyst is of utmost importance.^[29a]

It is appealing to attribute the origin of the reported *trans*-selective hydrolysis with a mutagenic lipase^[28] to a similar concept of steric constraint, as the enzyme is able to differentiate between fatty acids with linear geometry, namely

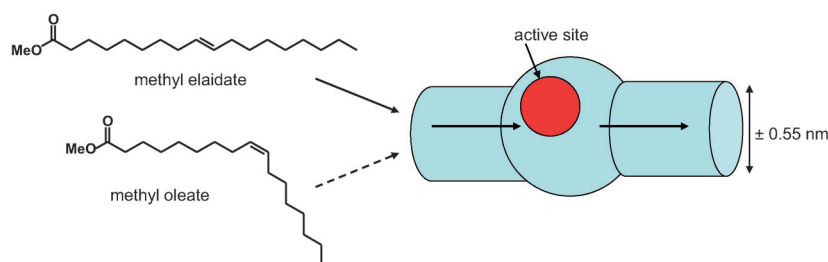


Figure 2. Removal of *trans* fatty acids in the presence of *cis* isomers by shape-selective hydrogenation over Pt-loaded ZSM-5 zeolite. *Trans*-selective hydrolysis with lipases that having a narrow acyl-binding tunnel occurs according to similar steric constraints.

saturated and *trans* fatty acids, and those with a bent geometry. The authors postulated that a narrow straight acyl-binding tunnel in the *trans*-selective lipase variants is responsible for the hindered access of *cis* fatty acids, thus allowing *trans* and saturated fatty acids to enter the active site more rapidly. This is conceptually similar to what happens in the pores of the ZSM-5 zeolite topology.

Despite the similarities of the concepts based on steric constraint, two important differences between the enzymatic and the chemocatalytic process should be noted. First, engineered lipases selectively hydrolyze not only *trans* but also saturated fatty acids in triglycerides, while the shape-selective Pt/ZSM-5 catalyst exclusively saturates *trans* double bonds in the triglyceride. Secondly, the ultimate product mixtures differ substantially. *Trans*-selective lipase produces free fatty acids, mainly consisting of *trans* and saturated isomers, along with the remaining *cis*-enriched mono-, di-, and triglycerides. To be useful, such a mixture requires additional fractionation/purification steps. The pool of free fatty acids could be used for transesterification purposes, while the essentially *trans*-free mono- and diglycerides are interesting food additives.^[32] In contrast, *trans*-selective hydrogenation of triglycerides over Pt/ZSM-5 zeolite produces essentially *trans*-free triglycerides, somewhat enriched in saturated fatty acid chains, which are of use for the immediate processing of food products.

The selective removal of *trans* isomers in diluted samples of partially hydrogenated vegetable oil (PHVO) with the shape-selective Pt/ZSM-5 catalyst and the best lipase-based variants are compared in Table 2. Interestingly, both process-

es are capable of removing *trans* isomers in a selective way from the pool of triglyceride molecules.

The combination of such shape-selective removal with new catalytic advances in hydrogenation catalysis should enable the production of essentially “zero *trans*” hydrogenated fat products. Therefore, further work on the removal of *trans* isomers from solvent-free PHVO samples should be encouraged. Also, it is currently very difficult to remove *trans* isomers from edible oils and fat samples containing low levels of *trans* isomers, namely in the range of 2–10 wt %.

5. Summary and Outlook

In order to obtain semi-solid fat products from vegetable edible oils with good stability and acceptable functionality, triglycerides with fatty acids that have a higher melting point need to be included. There are mainly two compounds that give structure to the solid fat products, namely *trans* and saturated fatty acids. In order to obtain low-*trans* fats with a good structure, *trans* fats need to be replaced (partly) by saturated fats, but preferably with a minimum impact on the total content of unsaturated fatty acids for nutritional reasons. Different saturated fatty acids with varying chain length are available and those with no adverse health effects on cardiovascular diseases should obviously be preferred. Debate is ongoing, but unambiguous evidence on CHD risk as a function of the intake of specific types of saturated fatty acids is still missing today.^[19a,b]

Next to the health issue, stability and physical properties are important parameters for the usage of the semi-solid fats in food products. Fractionation and/or interesterification are common unit operations for the production of a low or “zero *trans*” fat product with desirable physical properties. Tropical oils are ideal for such processing. Soybean oil, which is available in large quantities as a by-product from the feed industry, requires a hydrogenation process to reduce unstable polyunsaturated fatty acid content. Conventional sunflower and canola oil also need the stabilization process, but these oils are gradually replaced by oxidatively stable variants with high levels of oleic acid, albeit at a higher price.^[21]

While partially hydrogenated vegetable oils are largely substituted by fractionized and interesterified oils from tropical and modified plants, recent advances in catalytic hydrogenation show new opportunities, keeping it in the run as a major fat-modifying technology.^[4] First of all, selective

Table 2: Comparison of lipases and Pt/ZSM-5 catalyst in the removal of *trans* isomers in a PHVO sample.

Catalyst	Conv. [%]	$A_{cis}^{[a]}$	$A_{tr}^{[a]}$	$A_{tr}/(A_{cis}+A_{tr})$ [%]	Ref.
CAL-A WT	22	883	1203	58	[28]
F149D	11	3	78	96	[28]
T221H	5	0	48	> 100	[28]
I301H	12	0	107	> 100	[28]
Pt/ZSM-5 ^[b]	3	−4.1 ^[c]	35	> 100	[30]
Pt/ZSM-5 ^[b]	8	0.2	16	98	[30]

[a] Activity for the removal of *cis* and *trans* isomers, expressed as $\mu\text{mol min}^{-1}$, assuming an average MW of PHVO of triolein (885 g mol^{-1}).

[b] Reaction conditions: 5.5 g of a solution of PHVO (2 wt %) in octane, 0.1 g of Pt/ZSM-5 (1 wt % Pt), 65 °C, 6 MPa H_2 ; calculated after 15 and 60 min of reaction. [c] Initial formation of *cis* isomer. WT = wild type.

catalytic hydrogenation is the only process that allows selective conversion of unstable polyunsaturated fatty acids to more stable ones. With the exception of palm oil and some variants with high levels of oleic acid, most edible vegetable oils, such as soybean oil that is processed in food industry, are candidates for stabilization through selective hydrogenation. Formation of *trans* isomers, such as elaidic acid, is obviously unwelcome because of health reasons. Selective removal of *trans* fatty acids through stereoselective hydrogenation^[29a,30] or hydrolysis^[28] is an interesting option, and therefore highlighted herein, but avoidance of their formation during the hardening process is probably the ultimate challenge. New intelligent catalyst designs have opened unexplored possibilities to selectively hydrogenate vegetable oils into (semi-) solid fat products with essentially no *trans* fatty acids and preferably with a low content in undesired fully saturated triglycerides (SSS), thus minimizing adverse health effects without compromising the necessary optimal organoleptic food properties. This design relies on shape selective or pore mouth catalysis, involving the preferential hydrogenation of the fatty acid chain depending on its *sn*-position at the glycerol backbone.^[25a]

Being essentially *trans*-free, the regioselective hydrogenation catalysis may be an interesting option toward unique triglyceride compositions or even toward the synthesis of very specific fatty acids. For instance, the selective partial hydrogenation of polyunsaturated fatty acids, such as linole(n)ic acid, which are naturally located at the center position of the triglyceride, is now possible without significant formation of *trans* fatty acids. In another example, semi-solid fats with high levels of symmetric OSO (O = oleate; S = saturated fatty acid) may be produced from palm olein and oils with high levels of oleic acid. Or, at the level of the fatty acids, one might envision the synthesis of mono-unsaturated ω -3 fatty acids, such as C18:1 *c*15 at the preferred *sn*-2 position,^[33] as a thermostable substitute for the unstable ω -3 fatty acids, such as linolenic acid.

This essay presents a critical assessment of history, present status, and possible future developments in the hydrogenation of edible oils. It also presents recent advances in the design of catalysts for the partial hydrogenation of vegetable oil without the formation of *trans* isomers. Furthermore, it is meant to be a helpful guide for policy-makers, providing the society with nutritionally balanced and appetizing fat products, and industry with sustainable technologies. Governments should consider a full ban of *trans* fatty acids in food products, but they also should be aware that with the recent advances in catalyst development partial hydrogenation of vegetable oil should no longer be equivalent to *trans* isomer formation.

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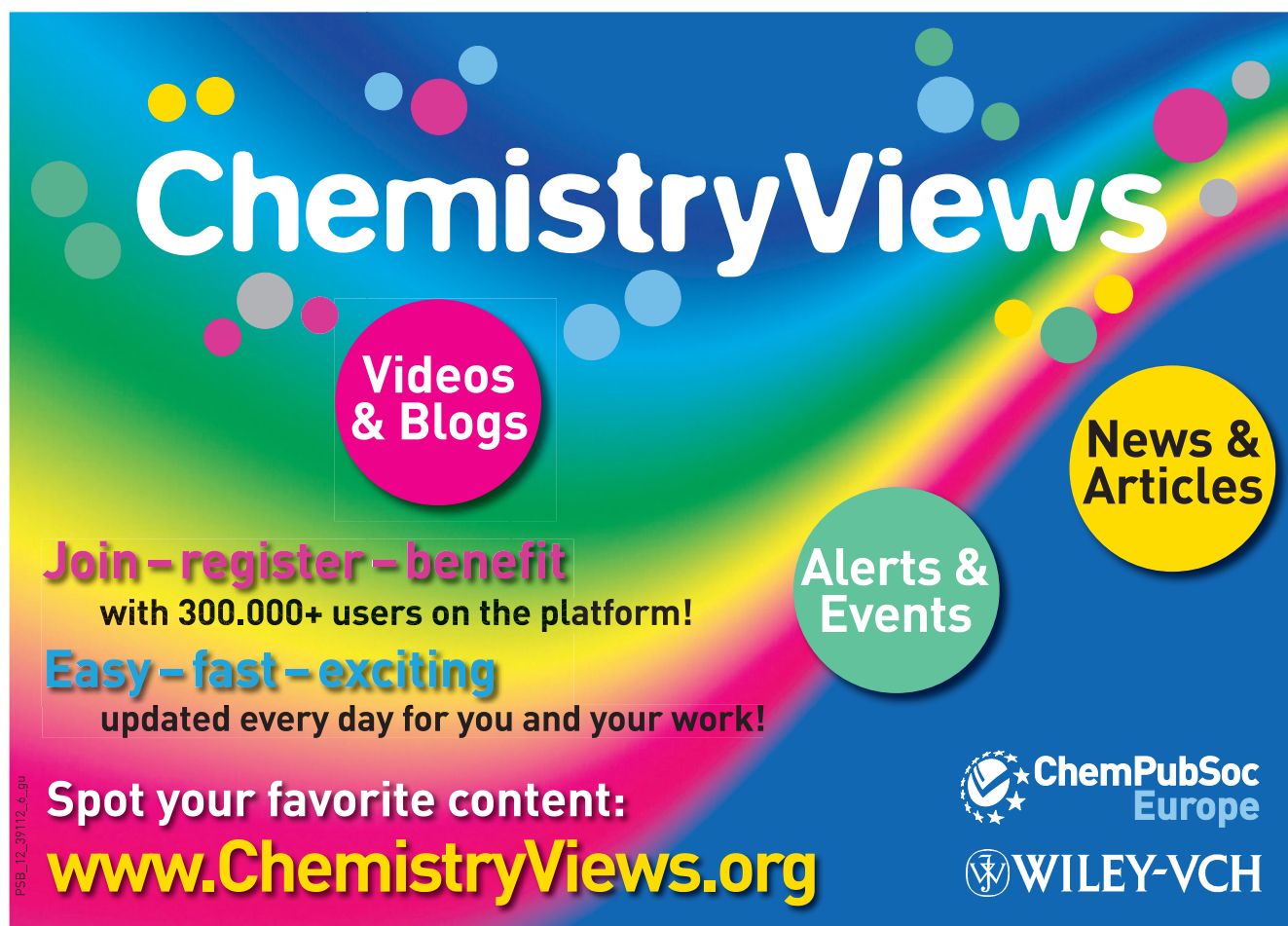
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